

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-06-0193

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Service and Communication, Washington, DC 20301-4070. That notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) 20 May, 2006		2. REPORT TYPE Final		3. DATES COVERED (From - To) July 1, 2002 - September 30, 2005	
4. TITLE AND SUBTITLE "Real-Time In-situ Characterization of Election-Beam-Induced Bulk Polymerizations"				5a. CONTRACT NUMBER F49620-02-1-0360	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Palmese, Giuseppe R.- Drexel University Klosterman, Don, A.. - University of Dayton				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER BAA 2001-4	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Drexel University 3141 Chestnut Street Philadelphia, PA 19104-2816				8. PERFORMING ORGANIZATION REPORT NUMBER 201024	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF, AFRL AF Office of Scientific Research 801 N. Randolph Street Room 732 Arlington, VA 22203-1977 Dr. Charles Lee - Program Monitor				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) USAF, AFRL	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approve for Public Release: Distribution Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The objective of this work was to develop a fundamental understanding of EB induced bulk polymerization of network forming systems and to apply this understanding for the rational development of improved EB cured materials. In order to obtain a fundamental understanding of the chemical and physical processes associated with EB curing and to develop a rational means for designing improved EB material systems, our research team focused on two major tasks. (1) Performing real-time in-situ characterization of EB cure kinetics for representative cationic and free radical cured systems and the development of appropriate mechanistically based cure models for the design of improved materials systems. (2) Development of a suite of real-time in-situ sensors to monitor major aspects of thermoset resin cure during EB irradiation that include chemical conversion, temperature, dose, dose rate, and residual stress. The scientific challenges were to elucidate the reaction pathways that occur during EB induced polymerization and to obtain a clear understanding of factors that govern final material performance.					
15. SUBJECT TERMS Electron Beam Curing, Composites, Cure Kinetics, Epoxy, Fracture Toughness					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Giuseppe R. Palmese
U	U	U	U	32	19b. TELEPHONE NUMBER (Include area code) 215 895 5814

**Real-Time *In-situ* Characterization of Electron-Beam-
Induced Bulk Polymerizations**

F49620-02-1-0360

Final Report

Period of Performance: 7/1/02 – 9/30/05

Final Performance Report

Period of Performance: 9/1/04 – 9/30/05

PI: Giuseppe R. Palmese

(215) 895-5814

palmese@coe.drexel.edu



Drexel University

Department of Chemical and Biological Engineering

3141 Chestnut Street

Philadelphia PA 19104

20060619047

1.0 Objectives

The objective of this work was to develop a fundamental understanding of EB induced bulk polymerization of network forming systems and to apply this understanding for the rational development of improved EB cured materials.

In order to obtain a fundamental understanding of the chemical and physical processes associated with EB curing and to develop a rational means for designing improved EB material systems, our research team focused on two major tasks.

- (1) Performing real-time *in-situ* characterization of EB cure kinetics for representative cationic and free radical cured systems. This entailed the development of appropriate mechanistically based cure models and the design of improved materials systems. In particular, a detailed understanding of the relationships among processing variables (time, temperature, dose rate, and composition) kinetic and thermodynamic processes, the formation of polymer networks and the resulting influence of these on material performance was obtained. Linking the processing and material variables to final behavioral characteristics in this manner provided the fundamental framework needed to design improved material systems.
- (2) In support of the first task, a suite of real-time *in-situ* sensors was developed to monitor major aspects of thermoset resin cure during EB irradiation that include chemical conversion, temperature, dose, dose rate, and residual stress.

The scientific challenges of this work were to elucidate the reaction pathways that occur during EB induced polymerization and to obtain a clear understanding of factors that influence final behavioral characteristics of e-beam cured systems.

2.0 Status of the Effort

The effort conducted by the team comprised of Drexel University and University of Dayton researchers is complete and has been successful in addressing the objectives of the program on numerous levels. The general research approach that was taken is summarized in **Figure 1**. The influence of processing and material variables on the EB induced polymerization by cationic and free radical mechanisms has been investigated. Of particular interest are the influences of time, dose rate, compositional impurities, and temperature on polymer microstructure and material performance. **This report summarizes the key findings of the entire program and highlights the research details of the effort conducted from September 1, 2004 to September 30, 2005.**

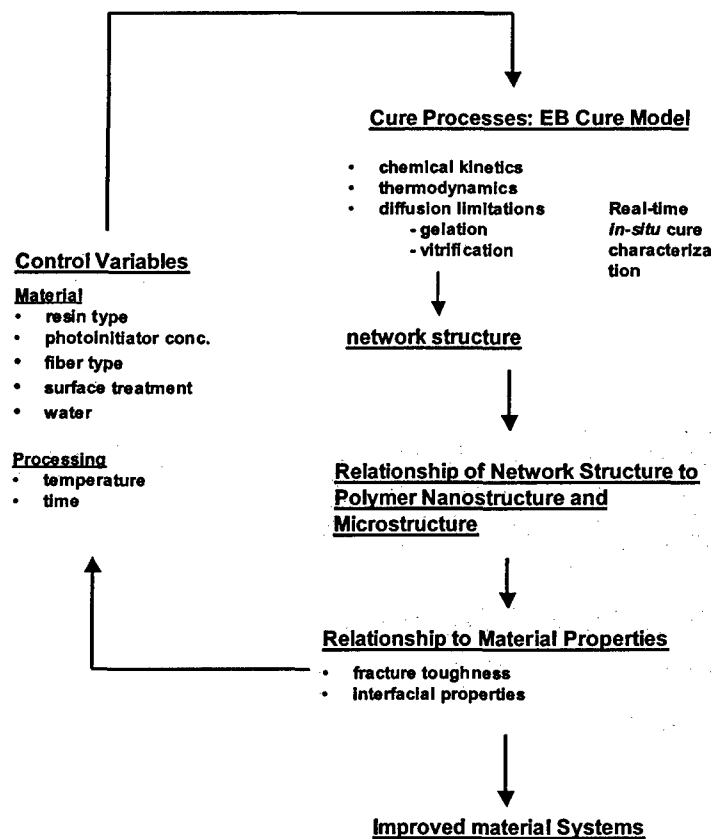


Figure 1: The general approach for tailoring the performance of thermosetting systems used in this program. The first step is to understand the relationships of material and processing control variables to kinetic (chemical and diffusive) and thermodynamic processes (i.e. phase separation) that lead to chemical conversion and network formation. This step requires the development of accurate and mechanistically based cure models that hinge on the ability to characterize cure processes *in-situ* and in real-time. The second step is to link the formation of network structures to the nanostructure and microstructure that dictate material performance. The last step is to relate these microstructures to material performance thus closing an “optimization loop” designed to develop improved EB materials.

3.0 Summary of Program Accomplishments

1. In-situ EB characterization techniques have been developed including fiber optic NIR, Raman spectroscopy, temperature control, calorimetry and dosimetry. A more detailed report of this work was given in the 03-04 performance report. Our accomplishments in this area can be summarized as follows.
 - o Installed sensor and ancillary equipment infrastructure in UDRI e-beam lab required for basic research studies, including thermocouple and fiber optic bus system, computer data acquisition and noise filters, Raman spectrometer and sample fixture, temperature controlled hot plate for

resin casting, gas purge lines, vacuum bagging pump, heater power line and digital controller, and electrical cables for various sensors such as dielectric and residual stress fixture.

- Completed a theoretical modeling study to verify the accuracy of thermocouples used to monitor the temperature of a polymer resin under e-beam irradiation. When using sufficiently small thermocouples and dose rates typical for composite curing, heat transfer will ensure that the thermocouple temperature is within 0.5°C of the immediately surrounding resin, which is well within the practical accuracy of thermocouples in general.
- Developed a fiber optic based in-situ near IR spectroscopy technique to monitor cure as a function of e-beam process variables. The method was used successfully to investigate the cure of cationically cured epoxies as well as free radically cured acrylates, methacrylates, and bismaleimides.
- Developed an e-beam calorimeter and associated data analysis procedures. The calorimeter operation has been demonstrated by measuring the cure rate for a model epoxy resin (PGE) under e-beam irradiation. The results revealed important differences in cure kinetics (both "light" and "dark") compared to kinetic models derived from real-time spectroscopic data.
- A low resolution Raman spectrometer and was installed and test fixture developed for real-time cure monitoring of a vinyl ester / styrene copolymer. Results indicated that conversion of each monomer could be monitored independently.

2. *In-situ* chemical kinetic studies were conducted on EB and UV induced polymerization of cationically and free radically cured e-beam systems

- Extensive studies have been conducted for cationically cured epoxies - DGEBA (diglycidyl ether of bisphenol A) and the monofunctional analog PGE (phenyl glycidyl ether) - that have led to a better understanding of cure behavior and factors that influence material behavior. Moreover, the results have allowed for the development of improved e-beam cured epoxy systems.
 - Studies of "light" and "dark" reactions were conducted to highlight the type of active center present in the chain polymerization reactions of epoxies and to obtain an understanding of the influence of discontinuous irradiation dose which is common practice when processing composites by e-beam.
 - The influence of water on the cure of cationically cured epoxies was investigated. This involved (a) the development of a NIR

cure monitoring method able to monitor epoxide, water, and hydroxyl concentration, (b) the development of a mechanistically based kinetic model for understanding the reaction pathways and for use in process models, - summarized in **Section 4.1** - and (c) an understanding of the influence of water on final polymer behavioral characteristics.

- Free radically cured systems have been evaluated. Particularly the copolymerization behavior of maleimide monomers with appropriate reactive diluents has been investigated. The results show that the reactivity of the diluent can be tailored so that mixtures with bismaleimide are stable at room temperature but polymerize readily upon EB exposure. In particular, we have investigated EB induced free radical copolymerization behavior of bismaleimide and the novel reactive diluent acrylomorpholine that has allowed the development of low temperature processable liquid molding resins with Tg as high as 370 C
3. Improved cationically cured epoxy systems that rival traditional thermally cured counterparts have been developed based on the detailed understanding of cure behavior outlined above and the discovery of a new class of chain extenders. The influence of chain extenders and novel comonomers based on THF ring opening chemistry on material behavior was investigated. The results show that the THF based comonomers are promising materials for improving the fracture toughness of EB epoxy systems. Materials have been developed that possess Tg ~190 C and Gic ~ 250 J/m² (note that this level of performance provides commercial viability for high performance composite applications)- **Section 4.2** provides a summary of the most recent key findings. Future work would entail using second phase toughening to further improve resin performance and a complete composite testing program.
- Exploratory work has shown that multiwall carbon nanotubes (MWCNT) can be modified using dry processes (EB irradiation in air) and that the degree of modification is controllable based on total dose. This can potentially provide an economical means of surface modification that does not require wet chemistry. **Section 4.3** provides the details of this work. Future work should focus on completely characterizing surface functionality, treatment of CNTs with other reactive gases, and the design of functional polymeric surface coatings via grafting methods.
 - Numerous beneficial interactions as summarized in **Section 7.0** have included joint experimentation with AFRL scientists as well as members of other research laboratories.

4.0 Details of Accomplishments and New Findings for 9-1-04 to 9-30-05

4.1 Influence of Water on Cationic Epoxy Polymerization – A Mechanistic Study

Summary

The purpose of this investigation is to gain further understanding of the influence of water on phenyl glycidyl ether (PGE) and diglycidyl ether of bisphenol A (DGEBA). A near infrared (NIR) spectroscopy technique reported earlier was further developed to perform real-time *in-situ* kinetic analysis of radiation induced, electron beam (EB) and UV, cationic polymerization of epoxy systems with water. NIR spectroscopy was used to quantify the concentration of water in PGE and DGEBA prior to cure. The chemical kinetics results indicate that the presence of water affects the polymerization of the epoxy systems by (a) the appearance of a pronounced retardation period, (b) an accelerated reaction following the retardation period when compared to “dry” systems, and (c) higher conversion at shorter times. A kinetic mechanism is proposed to explain this behavior and a model based on this mechanism is reported which was found to be in good qualitative agreement with experimental results.

Influence of water on PGE cationic polymerization via UV and EB radiation A spectroscopic investigation of the influence of water on the polymerization of PGE was carried out as described in a previous performance report. Real-time NIR spectra were analyzed by measuring water and epoxy peak heights as a function of time assuming a linear dependence of peak heights with concentration. Therefore, epoxy peak heights were normalized by the initial peak height and the resulting values are dimensionless concentration. Water concentration was determined using appropriate calibration curves described previously. Representative plots of epoxy concentration as a function of time for a number of initial water concentrations are given in **Figure 2** for UV and EB studies.

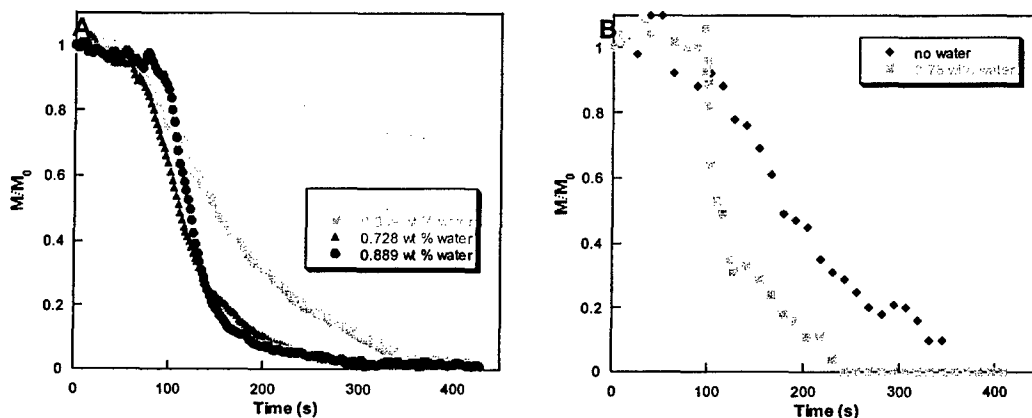


Figure 2: Comparison of PGE cure behavior for a number of initial water concentrations [UV (A) with 0.67pph initiator at 50°C and EB (B) with 1pph initiator at 50°C].

These plots show that the addition of water greatly influences the chemical kinetics of polymerization. The presence of water leads to an initial retardation of epoxy conversion that is followed by an accelerated rate of epoxy conversion relative to that of dry systems. **Figure 3** shows the consumption of water (peak height at 1908 nm) and the formation of hydroxyl groups (peak height minus initial peak height at 1436 nm) for a representative experiment indicating an inverse relationship between water consumption and hydroxyl group formation. **Figure 4** shows water and epoxy conversion data for "dry" and "wet" systems reacted under UV and EB irradiation. These plots show the temporal variation of water concentration where it is clear that a significant retardation in epoxy conversion occurs while the water is being consumed. When most of the water has been consumed, there is an apparent acceleration in epoxy reaction.

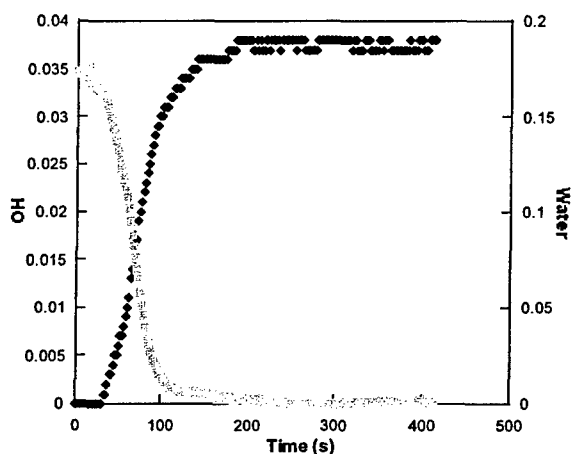


Figure 3: Representative concentration temporal profiles showing the inverse relationship between the consumption of water and the formation of hydroxyl peaks during cure.

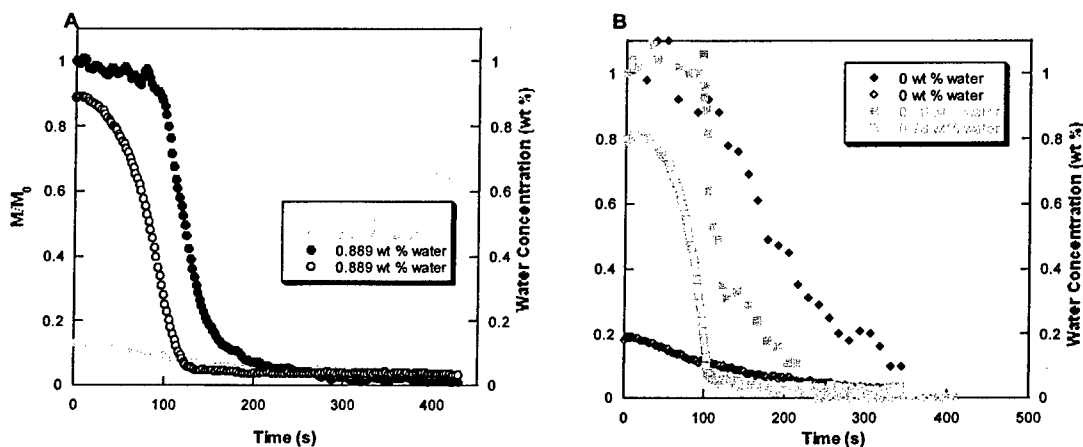
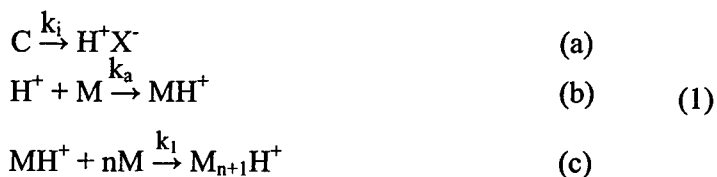


Figure 4: Temporal profiles for epoxy (closed symbols) and water (open symbols) conversion for the limiting cases of water for UV (A) and EB (B) -induced polymerization.

One possible condensed set of reactions describing the initiation and propagation of epoxy polymerization using photo-initiators is given by Equation 1. Equation 1(a) describes the generation of the super acid, Equation 1(b) is the reaction of the super acid with the monomer to form the activated monomer. Equation 1(c) represents the activated monomer-to-monomer reaction. With the assumptions that (i) termination does not occur, (ii) diffusion limitations are not important, and (iii) that there is a negligible concentration of hydroxyl groups present either initially or as the photo-initiator is consumed, this set of equations has been used successfully to describe the reaction of "dry" mono-functional glycidyl ethers such as PGE under continuous EB and UV irradiation.



However, the results given in Figure 4 show that epoxy reaction changes dramatically with the addition of water. The qualitative influence of water can be understood by the set of reactions given in Equation 2 that represent the reaction of water with the initial activated monomer species (a) and the formation of a new alcohol moiety with the regeneration of a new activated monomer (b) followed by the reaction of active species with these alcohols (c and d). In writing these reactions we assume that the concentration of hydroxyl groups formed from the photo-initiation is negligible. This is a valid simplification in that the concentration of hydroxyl groups formed from the water reaction is much greater than that obtained by initiation since the molar concentration of photo-initiator is much lower than the molar concentration of water investigated in this study. In this analysis we also ignore the reaction of water and

hydroxyl groups with higher molecular weight active centers. The explicit chemical reactions summarized by Equation 2 are given in Figure 5.

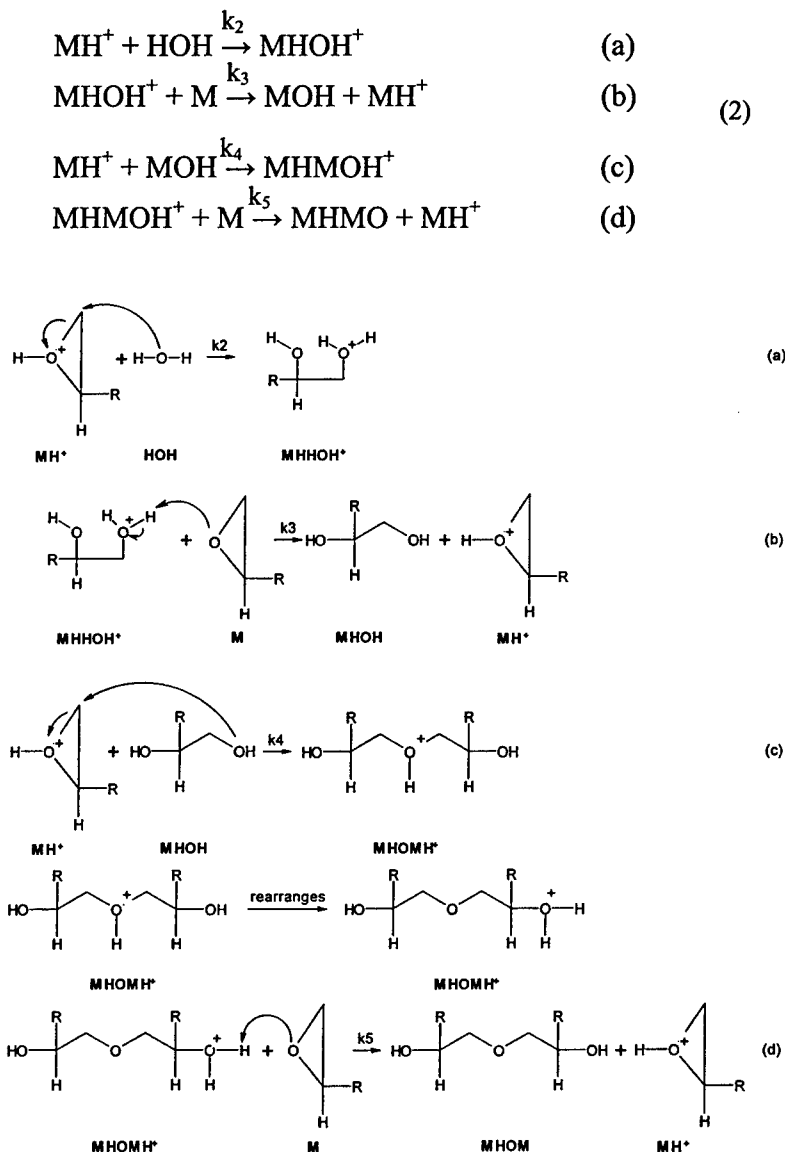
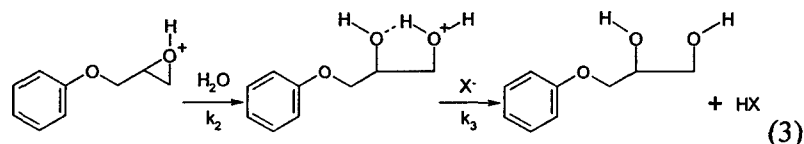


Figure 5: Cationic epoxy and water chemical reactions summarized by equation 1.

Our results show that the initial reaction of water is fast and appears to retard the reaction of epoxy. This would be possible if the reaction 3a proceeded much more rapidly than 3b. However, this by itself would not explain the eventual acceleration of the epoxy rate of reaction. Other researchers have attributed the slower initial conversion of the epoxy to the formation of a stable resonance structure. The subsequent release of the proton to initiate the next chain (Equation 2b) is hindered by a stable five-member ring system. Equation 3 shows the reaction of activated PGE with water to form

this stable five member ring that may cause the retardation by potentially "sequestering" propagating active centers.



Although reaction 2b may be slow compared to 2a, once the water is consumed not only will reaction 1b become important, but also reactions 2c and 2d of the alcohols from 2b with activated monomers. It is known that the reaction of such alcohols with active centers is faster than the reaction of epoxies with the active center. Hence, the continued generation of active centers through photo-initiation and the release of "sequestered" active centers with the concomitant formation of alcohols would result in an accelerated rate of epoxy conversion.

To test our reasoning the differential equations resulting from **Equations 1 and 2** were solved numerically and a parametric study was conducted to evaluate the importance of the relative values of the reaction rate constants. Previously obtained values of k_1 and k_a were used (note that $k_i > k_a$). The water reaction data at short times was used to determine that k_2 was eight times greater than k_1 . By adjusting the rest of the parameters based on our previous discussion so that $k_5 \gg k_2 > k_4 > k_1 \gg k_3$ it was found that the observed influence of water on the cationic polymerization of epoxies can be replicated qualitatively. This is shown in **Figure 6** where both the retardation and acceleration are seen when comparing reaction cases involving "dry" and "wet" reactions. It was also found that the extent of the retardation period can be controlled by appropriately adjusting the rate constants.

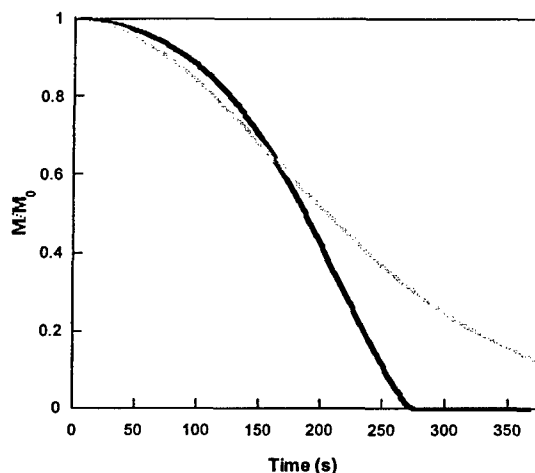


Figure 6: Kinetic model of epoxy with water (black line) and without water (gray line) in the system showing qualitative agreement with experimental results.

Conclusions

An *in-situ* fiber optic spectroscopic technique was used for quantifying water concentration in epoxy samples, and data was presented concerning the influence of water on the UV- and EB-induced polymerization behavior of PGE and DGEBA. The presence of water in PGE and DGEBA was observed to significantly alter the cure behavior in important ways. There is a pronounced retardation period followed by an accelerated reaction regime relative to that observed for "dry" systems. A mechanism was proposed to explain this behavior. It is based on the relatively faster reaction of water with an activated monomer to form a relatively stable five member ring system compared to the reaction of epoxy with the activated monomer. The observed acceleration is thought to result from the slow regeneration of active centers and the generation of alcohol moieties from these ring structures as water reacts to completion. A kinetic model was used to test the proposed mechanism and the results were found to be in excellent qualitative agreement with the observed behavior. Because the water is consumed during the polymerization, it must alter the resulting network structure. In previous studies under this program water was found to decrease the T_g of the epoxy network significantly and also to substantially increase its fracture toughness.

4.2 Novel Monomer Systems – Improved Resin and Composite Properties

Summary

The overall objective of our work was the design of improved EB cured epoxy systems based on diglycidyl ether of bisphenol A (DGEBA). One method for designing such systems is the use of network modifiers. Herein we report the development of a new class of chain extenders based on the ring opening copolymerization of tetrahydrofuran (THF) with DGEBA. In last years performance report we presented the successful copolymerization of THF with DGEBA induced by EB in the presence of an appropriate photoinitiator. THF was found to increase fracture toughness with a concomitant decrease in glass transition temperature. Additionally, THF presents practical processing difficulties associated with its high volatility. A series of novel THF functional comonomers was designed to mitigate the aforementioned drawbacks associated with THF. These include difunctional (first reported last year - GP3 and GP4) and trifunctional monomers possessing THF functionality which are the subject of this report. Last year's data as summarized in the penultimate performance report show improved fracture toughness with a resulting decrease in T_g . With the use of trifunctional epoxy modifiers it was found that the fracture toughness of EB cured DGEBA systems can be improved almost five fold with minimal loss of T_g . Moreover preliminary results indicate that composite properties can also be improved using these comonomers.

Background

The focus of this portion of the work is to design improved EB cured DGEBA systems by modification with appropriate chain extenders designed to impart the appropriate level of network flexibility while maintaining glass transition temperature requirements. This is shown schematically in **Figure 7** where tailoring the network is accomplished by copolymerization with other monomers that increase the molecular weight between crosslinks. This method also allows for varying chain flexibility to adjust material properties.

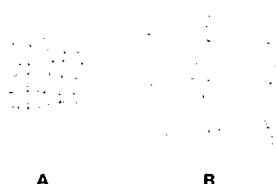


Figure 7: Schematic representation of a highly crosslinked network (A) and homogeneously modified by copolymerization with a chain extender (B).

In previous work we investigated factors influencing the polymerization of epoxy resins and found that hydroxyl groups, specifically alcohols, can play an important role in polymerization of epoxies. Alcohols with $-OH$ groups positioned on different carbon atoms of the chain (primary, secondary, and tertiary) were studied to determine their influence on the network formation of DGEBA via cationic polymerization. We concluded that the intrinsic reactivity of alcoholic species with the active center relative to that of a glycidyl ether moiety with active centers changed the degree to which the network structure was disrupted. This showed that the potential exists to tailor epoxy network formation in such systems by introducing specifically designed comonomers with appropriate $-OH$ functionality.

As described previously we have investigated the influence of water on DGEBA cationic polymerization induced by EB and found that likewise the addition of water affects the cure behavior of DGEBA and the formation of the network structure. In such cases an initial retardation period followed by acceleration in the epoxy conversion was observed. Increased concentrations of water caused longer delays and increased epoxy conversion. Consumption of water during the polymerization indicated that the resulting network structure was altered. We have shown that the addition of water decreased the glass transition temperature significantly from $\sim 190^{\circ}C$ for "dry" epoxy to values as low as $170^{\circ}C$ for systems modified with 1 wt% water. This decrease in T_g was accompanied by a modest increase of fracture toughness from a G_{IC} of $56 J/m^2$ for the "dry" system to $G_{ICs} \sim 140 J/m^2$ for the material modified with water. These results suggest that the increase of G_{IC} resulted from the decrease of cross-link density associated with chain transfer reactions with water.

Recently, other chain extending strategies have been explored to tailor the network structure and improve mechanical properties. The most interesting of these is the use of ring-opening comonomers based on five member ether rings like tetrahydrofuran as shown schematically in **Figure 8**. We have discovered that with the appropriate photoinitiator THF copolymerizes readily with DGEBA epoxies. Such copolymerization leads to the insertion of 4 methylene linkages in the crosslinked DGEBA structure.

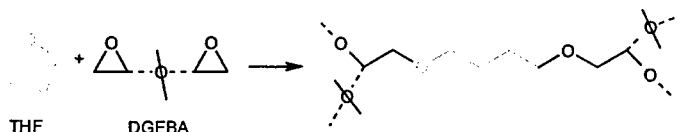


Figure 8: Proposed ring opening reaction of DGEBA and THF resulting in the insertion of a flexible chain.

Mechanical property evaluation of THF modified DGEBA showed that the G_{IC} value increased from 56 J/m² to 217 J/m² when 10 wt% THF was used. However, drawbacks associated with the use of THF include high volatility and significant T_g depression. In this work we present a series of novel THF functional comonomers designed to mitigate the aforementioned drawbacks associated with THF. These monomers include difunctional and trifunctional systems that are designed not only not to be volatile but also to impart higher T_g . The synthesis of these monomers is described below.

Synthetic Procedures

Materials The chemical structures of materials used in this investigation are given in **Table 1**. These include the materials used to synthesize THF functional comonomers. Diglycidyl ether of bisphenol A (DGEBA) (Resolution Epon 825) was used in this investigation. Water was removed from this material using 4Å molecular sieves (Aldrich Chemical Company, Inc) conditioned at 120°C for 12 hours prior to use. Such drying limits water concentration to below 0.1% in the DGEBA. Diphenyl iodonium hexafluoroantimonate (Applied Poleramics CD1012) was used as the photoinitiator. The chain extender tetrahydrofuran (THF) was obtained from Aldrich ($\geq 99.0\%$, H₂O <0.05%; inhibited with 250 ppm butylated hydroxytoluene) and was also dried using molecular sieves. Tetrahydro-2-furoic acid (Aldrich: 97%; inhibited with 250 ppm butylated hydroxytoluene) was used to synthesize difunctional and trifunctional chain extending comonomers based on the esterification reaction with DGEBA and triglycidyl ether of trisphenol-methane (Tactix 742) respectively.

Table 1: The chemical structures of the materials used in this experimental work.

Material	Chemical Structure
Diglycidyl ether of bisphenol A (DGEBA). EPON 825	
Triglycidyl Ether of Trisphenol-methane (Tactix 742)	
Diphenyl iodonium hexafluoroantimonate CD1012	
Tetrahydrofuran (THF)	
Tetrahydro-2-furoic acid	

Preparation of DGEBA and THF Systems DGEBA and various concentrations of THF ranging from 1 wt% to 20 wt% were premixed before adding the CD1012 photoinitiator. Samples were kept in a sealed dark container at 60°C until cured.

Preparation of DGEBA and Tetrahydro-2-furoic Acid Systems A new difunctional monomer (GP3) with THF functional end groups was synthesized by the esterification reaction shown in **Figure 9**. DGEBA and tetrahydro-2-furoic acid in stoichiometric quantities (1:2 molar ratio) were mixed and reacted at 60°C using 1 wt% AMC-2 catalyst (Aeroiet Fine Chemicals), Samples were kept in a sealed dark container at 60°C for two hours.

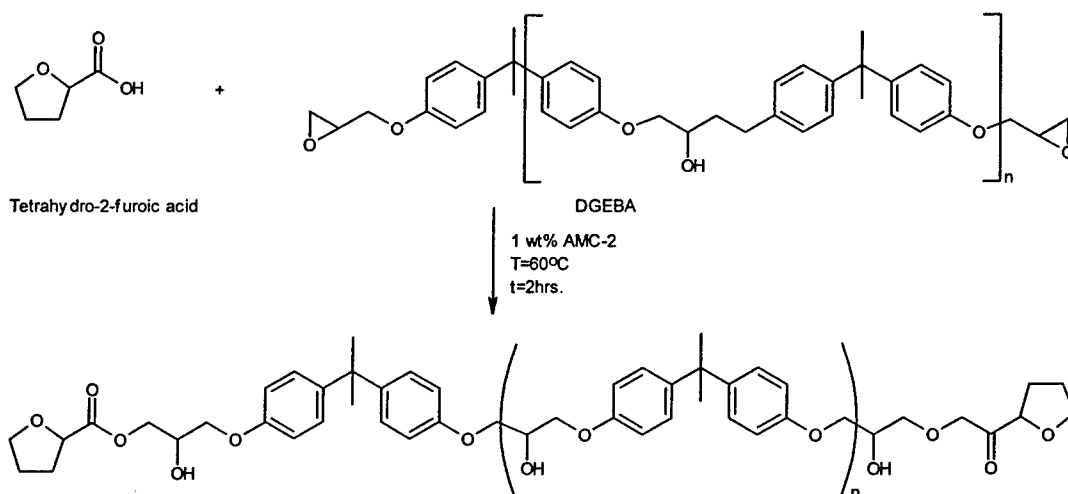


Figure 9: Esterification of tetrahydro-2-furoic acid and DGEBA using AMC-2 catalyst to synthesize the chain extender (GP3).

Preparation of Tactix 742 and Tetrahydro-2-furoic Acid Systems A new trifunctional monomer (GP5 shown in Figure 10) with THF functional end groups was synthesized from the esterification reaction similar to GP3 synthesis. Tactix 742 and tetrahydro-2-furoic acid in stoichiometric quantities (1:3 molar ratio) were mixed and reacted at 60°C using 1 wt% AMC-2 catalyst. Samples were kept in a sealed dark container at 60°C for two hours.

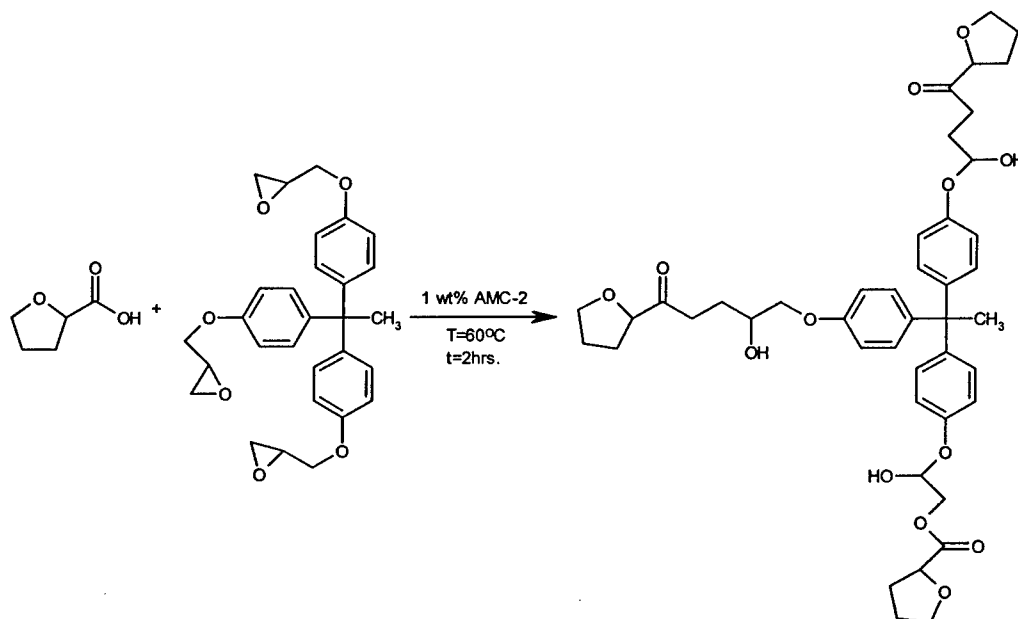


Figure 10: Esterification of tetrahydro-2-furoic acid and Tactix 742 with AMC-2 catalyst to synthesize chain extender (GP5).

Composites Processing DGEBA and 35 wt% GP3 were mixed with 1pph CD1012 and kept in a dark sealed glass container at 60°C. A wet hand lay-up technique was used to fabricate composite plaques. In this method 5HS 12k tow AS4 carbon fabric with G' sizing was used for reinforcement. In our experiments, eight layers of carbon fiber fabric were used to prepare the composites and all fabric layers were aligned in the same direction. After lay-up the system was bagged and a vacuum was applied. Cured composite fiber volume fraction was ~ 55%.

Sample Irradiation Neat resin samples were prepared using DGEBA with various concentrations of our three comonomers (THF, GP3, and GP5). The resin mixtures were transferred to a mold and then covered with a clear plastic film to prevent water absorption. EB cure was performed at the University of Dayton Research Institute Laboratory for Research on Electron Beam Curing of Composites. The EB machine is a 3.5 MeV EB accelerator specifically designed for irradiating samples in a controlled manner. The samples were irradiated as follows: 25 pulses/second, 60% scan width, 150 mA/pulse, and 3 kGy/pass for a total dose of 54 kGy. Resin plaques were post-cured up to a temperature of 150°C. Composites were cured by EB using the same irradiation schedule and were post cured up to a temperature of 200°C.

Results and Discussion

This work addresses the influence of THF containing comonomers on the performance of DGEBA systems. The first part of this section reports results of the investigation regarding the copolymerization of DGEBA and THF with particular emphasis on mechanical properties. The second part explores the use of novel chain extenders based on the esterification of DGEBA and Tactix 742 with tetrahydro-2-furoic acid resulting in difunctional and trifunctional THF endcapped comonomers respectively. The final part of this section summarizes preliminary data concerning composite behavior.

Chain Extension with Tetrahydrofuran New chain extenders were explored to tailor the network structure and improve mechanical properties of DGEBA systems cured cationically via EB. As mentioned in the introduction we have discovered that THF copolymerizes readily with DGEBA under EB irradiation and in the presence of a photoinitiator such as CD 1012. We presume that a tetramethylene ether grouping is added to the crosslinked network comprised primarily of DGEBA via ring opening of the THF molecule. This would necessarily result in a decreased crosslink density and potentially higher fracture toughness. In fact, our results show improved mechanical properties. At 10 wt% THF in DGEBA, the G_{IC} value increased almost by a factor of four: from 56 J/m² for neat DGEBA to 217 J/m² for the modified system. However the T_g of our systems suffered a very significant loss of T_g from 190°C for neat DGEBA to 111°C. Some of the loss could be a result of plasticization due to unreacted THF remaining in the system. However, after postcuring it is expected that unreacted THF will have been removed and no appreciable weight loss was observed. The high volatility of THF

presents a practical problem in its use and application to commercial processes. And, while the decrease in T_g can be somewhat curtailed by reducing the concentration of THF used, the dangers associated with THF evolution cannot. It was hypothesized that using THF as reactive endgroup on monomers possessing similar chain structure to DGEBA would result in toughened systems with higher T_g and in monomers with vapor pressure similar to that of DGEBA. The next section explores this possibility using such difunctional and trifunctional monomers.

Synthesis and Application of Chain Extenders by Esterification of DGEBA and Tetrahydro-2-furoic acid A new monomer, GP3, was synthesized by the esterification of DGEBA with tetrahydro-2-furoic acid as described in the experimental section and shown in Figure 3. This reaction adds THF functionality to the ends of DGEBA. DGEBA was mixed with GP3 at 20 wt% and 35 wt% loading and cured according to the procedures described earlier. The properties of the resulting polymers as obtained by DMA analysis and fracture toughness measurements in comparison to neat DGEBA polymers are given in Table 2. In both cases fracture toughness increased substantially with a concomitant decrease in T_g . The drop in T_g is significantly less than that observed for pure THF modification. In fact, 35 wt% GP3 corresponds roughly to the molar concentration of THF moieties found in 10 wt% THF modified DGEBA systems. Thus the comparison of 35wt% GP3 with 10 wt% THF shows a significant increase in T_g as well as slightly improved fracture toughness value. A likely explanation for this behavior is that the use of difunctional GP3 places a crosslink between two tetramethylene ether groupings in the resulting network structure. A second interesting observation is that the 20 wt% GP3 system possesses a T_g similar to that of DGEBA modified with 1 wt% water and a similar fracture toughness to that system

Table 2: Fracture toughness and T_g values for neat DGEBA and GP3 modified DGEBA

	$T_g(^{\circ}\text{C})$	$G_{IC} (\text{J/m}^2)$
Epoxy	190	56±7
20wt% GP3	169	146±19
35wt% GP3	131	275±33

These results indicate the potential for improving the mechanical properties of EB cured DGEBA systems. The challenge remains to improve fracture toughness with minimal or no loss in other properties, particularly T_g .

Synthesis and Application of Chain Extenders by Esterification of Trifunctional Epoxies (Tactix 742) with Tetrahydro-2-furoic acid Based on the results obtained for the difunctional THF endcapped system described in the previous section, analogous trifunctional systems were considered with the notion that these should result in higher

T_g materials when used as modifiers for DGEBA. Tactix 742 is a well known trifunctional epoxy that is commonly used for higher T_g applications compared to DGEBA. A new monomer, GP5, was synthesized via the esterification of DGEBA with tetrahydro-2-furoic acid as described above and shown in Figure 10. This reaction adds THF functionality to the ends of the trifunctional epoxy resulting in a modifier with three THF functional groups. DGEBA was mixed with GP5 at 1, 5 and 10 wt% loading and cured via EB according to the procedures described earlier. The properties of the resulting polymers as obtained by DMA analysis, flexural testing and fracture toughness measurements in comparison to the neat DGEBA polymer are given in Table 3.

The T_g of the modified DGEBA systems was found to be only slightly influenced by GP5 loading. Moreover the loss behavior observed by DMA and given in Figure 11 for the series of GP5 modified samples shows not only a nearly unchanged T_g but also a sharper transition indicating the existence of a more homogeneous network for systems containing higher concentrations of GP5.

Table 3: Mechanical properties of DGEBA modified using GP5 at various concentrations.

	T_g (°C)	G_{IC} (J/m ²)	Flexural Properties	
			Strength (ksi)	Modulus (ksi)
Neat Epoxy	190	56±7	8.9±0.8	344±10
1% GP5	180	167±29	10.0±0.9	334 ±14
5% GP5	187	186±18	10.1±1.0	336 ±18
10% GP5	180	250±42	10.7±1.0	334 ±13

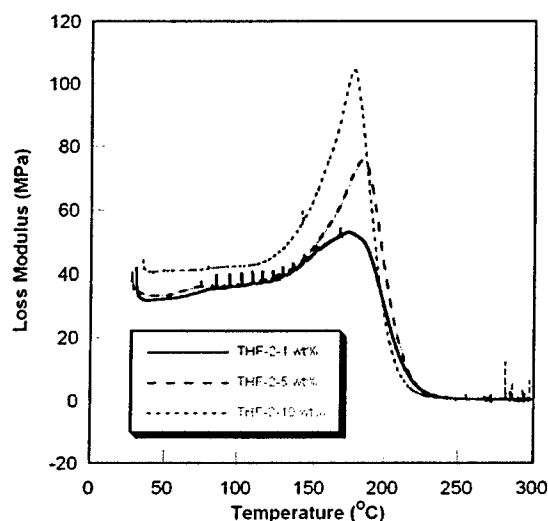


Figure 11: Dynamic mechanical behavior of DGEBA modified using THF trifunctional chain extenders.

The results of flexural testing show that the modifier has no influence on the flexural modulus of the material but that a significant increase in the flexural strength was obtained for all GP5 modified materials. A large, almost five-fold, improvement in fracture toughness was observed for the DGEBA modified with only 10 wt% GP5. This is a striking result given that there was not an accompanying significant loss in T_g . Moreover it suggests that it is possible to improve the properties of cationically EB cured DGEBA based epoxy systems without the loss of other important material properties.

Composite Properties Preliminary data concerning the properties of carbon fiber composites fabricated using a wet layup technique and cured by EB suggest that modification of DGEBA resin with the THF functional monomers like GP3 and GP5 may improve interlaminar shear behavior as measured by SBS tests. The SBS strength of neat DGEBA – carbon fiber composites using G' sized 5HS AS4 fabric was 6.0 ± 0.4 ksi. This is a typical result for EB cured epoxy systems and is one of the principal shortcomings associated with such materials. A similarly fabricated composite using DGEBA modified with 35 wt% GP3 as a matrix was found to have SBS strength of 7.5 ± 0.2 ksi which is a considerable improvement that further illustrates the potential of THF functional modifiers.

Conclusions

One of the major drawbacks associated with EB curing of DGEBA based systems is the poor fracture toughness obtained for such materials. In this work new chain extending modifiers were explored to tailor the network structure and improve mechanical

properties of DGEBA epoxies cured cationically via EB. It was discovered that THF copolymerizes readily with DGEBA under EB irradiation and in the presence of a photoinitiator such as diphenyl iodonium hexafluoroantimonate. We presume that via the ring opening of the THF molecule, a tetramethylene ether grouping is added to the crosslinked network comprised primarily of DGEBA. This results in lower crosslink density (lower T_g) and higher fracture toughness. In order to maintain T_g while improving fracture toughness a number of novel difunctional and trifunctional monomers were developed based on endcapping difunctional and trifunctional epoxies with THF moieties via appropriate synthetic procedures. These monomers were used as modifiers of DGEBA in the range of 1-35 wt%. All combinations increased fracture toughness considerably and in the case of the trifunctional system at 10 wt% loading, fracture toughness was improved almost five-fold with little effect on T_g resulting in a material with G_{Ic} of 250 ± 42 J/m² and a T_g of 180 C. The path taken to improve DGEBA based resins is summarized in Figure 12. Moreover, preliminary results suggest that the resin improvements also translate into improved composite properties.

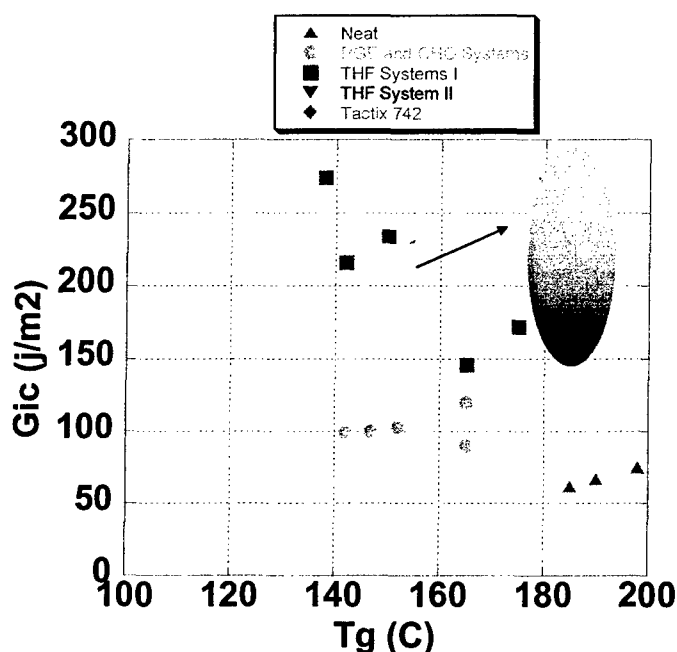


Figure 12: Plot showing the development of high T_g - high toughness systems based on THF functional monomers. The circles represent materials modified with OH functional linear polymers of Cyclohexyl oxide and PGE. These do not show significant improvement in fracture toughness but great reduction in T_g . The squares show results of THF modified systems (the group with higher fracture toughness but lower T_g) and THF functional DGEBA systems. These show general improvement over systems modified with hydroxyl functional polymers. The trifunctional THF functional modifiers represented by the shaded grouping of points show high fracture toughness and T_g .

4.3 Surface Modification of Carbon Nanotubes by E-beam

Summary

The development of nanotube-based polymer composites with improved mechanical properties and electrical conductivity requires the covalent dispersion of carbon nanotubes to utilize their stress transfer capabilities. Covalent dispersion of nanotubes therefore requires the functionalization of their surface to interact with solvents or monomers. In this work, we have developed a novel method of nanotube surface modification in which dry MWNT are irradiated with a high-energy electron-beam (EB) in ambient air environment. Raman spectroscopy was performed to characterize the influence of EB irradiation on nanotubes, namely, variance of the disorder, or D band ($\sim 1360\text{ cm}^{-1}$) with respect to the graphitic, or G, peak ($\sim 1580\text{ cm}^{-1}$). Spectra show increased deformation to the graphitic structure, as well as increased strain on the carbon-carbon bonds, weakening the nanotube. Transmission Electron Microscopy (TEM) confirms that nanotubes remain intact despite high EB dose. In addition, minimal surface deformation and length reduction occurred on irradiated MWNT.

In this communication, we report the use of high-energy electron beam (EB) irradiation as a new and potentially less destructive method of nanotube modification. By subjecting nanotubes to varied doses of EB irradiation under ambient conditions, we have discovered interesting behavior of nanotubes subjected to EB. In this study, Raman Spectroscopy has been used to characterize MWNT at both pristine state (raw) and after various EB irradiation doses. Characterization of the level of molecular deformity in irradiated nanotubes will provide insight into further functionalization of nanotubes best suited for large-scale materials processing applications. In addition, irradiation can serve as an alternative initiation step for current chemical functionalization methods such as those required for amino-functionalized nanotubes.

Materials All MWNT used for EB irradiation were commercially produced by electric arc discharge method and supplied by SES Research (purified). MWNT diameters ranged from 10-20 nm, as confirmed by our own TEM studies. Electric arc-produced MWNT were compared with commercial amine-functionalized MWNT, produced by carbon vapor deposition (CVD) and functionalized with ball-milling in ammonia.

EB Irradiation In this investigation, EB irradiation was performed with a research-grade linear accelerator housed at the University of Dayton Research Institute (UDRI). Separate MWNT samples, each containing 20 – 50 mg dry MWNT powder, were irradiated in normal atmospheric environment at 3.5 kGy/min under an EB operating at 3.5 MeV. MWNT samples were irradiated for various times – achieving doses ranging from 5-1000 kGy - to achieve the desired EB doses. The use of EB as a new modification method is illustrated in Figure 13. As MWNT are exposed to EB irradiation, active

centers are created. These active centers can then be functionalized to hold "R" chemical groups to be used in dispersion processes.

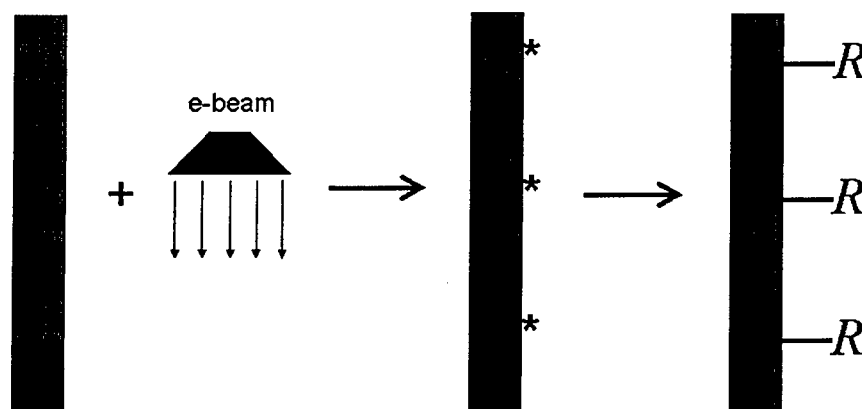


Figure 13: High-energy EB modification of MWNT produces active centers capable of further functionalization.

Raman Spectroscopy Pristine and EB-irradiated MWNT underwent Raman characterization (RM1000, Renishaw, Inc.) to determine the level of deformation in their graphitic structure. A total of 100 scans were taken of each of ten nanotube samples. Samples were characterized with a Renishaw 1000 Raman Spectrometer. An Ar⁺ ion laser, 514nm (2.41 eV), was used. Incident and scattered beams were focused with a 50x objective and laser spots with resolutions as low as 2μm. All tests were performed at room temperature.

E-Beam Irradiated MWNT Structural deformation was characterized using Raman spectroscopy. Specifically, the disorder (D) and graphitic (G) peaks were analyzed to determine the extent of deformation of EB-irradiated MWNT compared to pristine MWNT. As the spectra illustrate in **Figure 14**, a heightened D peak is apparent in the range of 1320 – 1375 cm⁻¹. Also apparent is a lowering of the G peak at 1585 cm⁻¹. This behavior is indicative of higher extent of surface modification, increased deformation to the nanotube structure, and a change from the normal sp² hybridization in pristine MWNT to sp³ within the irradiated sample.

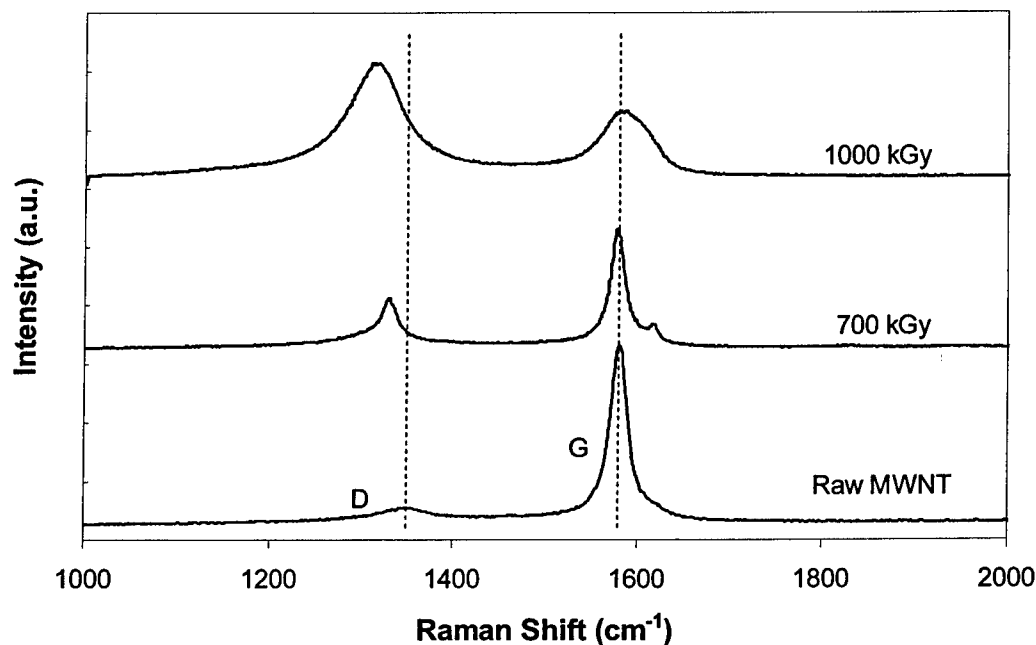


Figure 14: Raman spectra from raw and EB-irradiated MWNT. Raman spectra obtained using Ar⁺ ion 514.5 nm (2.41 eV) laser excitation with ~2 μm spot size. Heightened D band is observed with increasing EB dose. Broadening and wavelength shift of the D peak is also observed in MWNT exposed to EB.

In the spectra, a heightening of the D band correlates with a lowered graphitic (G) peak. Raman spectra of raw MWNT show an intense G peak accompanied by a shallow D peak. As EB dose increases, a heightening of the D peak and lowering of the G peak are observed. To normalize this relationship, D:G peak heights were calculated and plotted in Figure 15 for Raman spectra obtained at each EB dose level. From the plot, there is a general upward trend between EB dose and D:G ratio that can also be correlated with changes in the nanotube structure.

Also observed is a horizontal shift of the D band to lower frequency with increased EB dose. Figure 13 shows a downshift in the D-band frequency by 55 cm^{-1} , while the G peak remains at 1585 cm^{-1} . Decreasing D band frequencies seen in the spectra were plotted in Figure 16. From this plot, an asymptotically decreasing trend in D band frequency is observed with increasing EB dose. This frequency shift may be a result of strain placed on carbon-carbon bonds, induced by irradiation, upon which, bonds are elongated, thus becoming weaker.

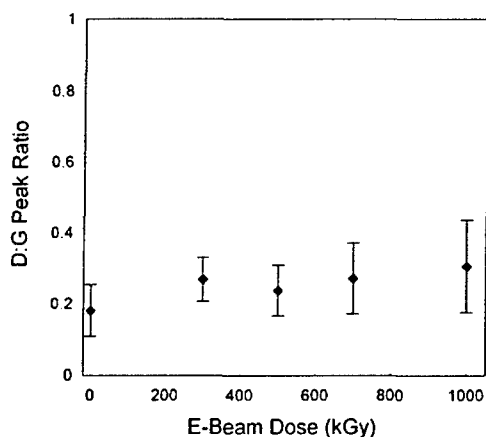


Figure 15: Ratio of D:G peak heights with respect to EB dose.

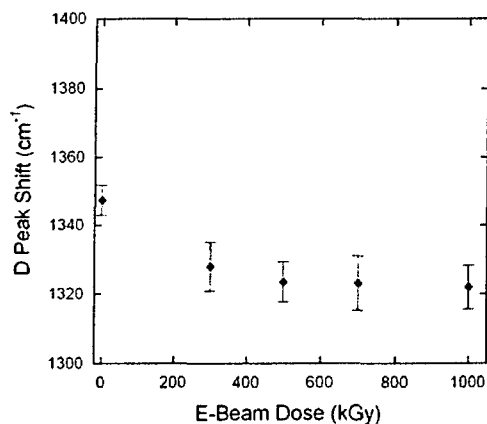


Figure 16: D band horizontal (frequency) shift with respect to EB dose.

Conclusions

In summary, the surface modification of MWNT, performed via high-energy EB irradiation, has proved an effective, but mild, modification technique. Characterization via Raman Spectroscopy has illustrated the extent of modification and low incidence of deformation to the nanotube's structure when compared with current functionalized nanotubes. Nanotubes exposed to EB have shown a consistent increase in deformation as EB irradiation dose increases. This provides a basis for assessing the optimum level of deformation (due to changes in carbon atom state of hybridization) for the functionalization of nanotube surfaces while maintaining the graphitic structure. The high-energy EB irradiation may therefore allow for chemical functionalization of nanotubes without total destruction of the nanotube or significant decrease in its mechanical and material properties, thus allowing for the covalent dispersion into various media that provide increased strength, elasticity, and electrical conductivity to material systems.

5.0 Personnel Supported

Faculty:

Giuseppe R. Palmese (Drexel University)

Don A. Klosterman (UDRI)

C. William Lee (UDRI)

Graduate Students:

Jihean Lee (PhD, Drexel – expected completion September 2006)

Xing Geng (PhD, Drexel – graduated June 2005)

Maria Cecilia Evora, (PhD, University of Dayton -Fulbright Scholar, Brazil, expected graduation July 2009)

Anish Desai (M.S. University of Dayton)

Sabari P. Mopidevi (M.S. University of Dayton)

Phani Kumar Putravu (M.S. University of Dayton)

Undergraduate Student:

Adam Wise (Summer BS student from RPI)

Mary Sullivan (Drexel BS-PhD – nanotube modification)

Gila Stein (Drexel BS)

High School Student:

Amy Peterson (Illinois Math and Science Academy now an undergraduate at Drexel)

6.0 Publications (*related only to EB curing and processing*)

Journal Articles:

1. X. Geng and G.R. Palmese, "Cyanate Ester - Bismaleimide Interpenetrating Polymer Networks via Electron Beam Irradiation." *Polymer*, (manuscript prepared)
2. X. Geng and G.R. Palmese, "Effects of Diluent Reactivity on Electron Beam Polymerization of Bismaleimides," *Journal of Applied Polymer Science*, (manuscript prepared)
3. X. Geng, G.R. Palmese, "Electron Beam Induced Free Radical Copolymerization of N-Acryloylmorpholine and N-Phenylmaleimide," *Journal of Polymer Science, Polymer Chemistry*, (manuscript prepared)
4. J. Lee and , A. Johnston, G.R. Palmese, "Dark and Light Reactions of Epoxy Cationic Polymerization Induced by Electron Beam," *Journal of Polymer Science, B: Polymer Physics*, (manuscript prepared).
5. J. Lee and G.R. Palmese, "The Influence of Water on the Cure Kinetics and Properties of Polymers based on Glycidyl Monomers Polymerized Via Irradiation ," *Polymer*, (manuscript prepared).

6. Desai, A., D. Klosterman, C.W. Lee, "Development of a Real-Time Calorimeter for Monitoring Electron Beam Curing of Polymer Resins," manuscript in development, February 2006.
7. E. J. Robinette and G.R. Palmese "Synthesis of Polymer-Polymer Nanocomposites Using Radiation Grafting Techniques," *Nuclear Instruments and Methods in Physics Research B*, 236, 216-222 (2005).
8. Klosterman, D., R. Chartoff, T.Tong, M.Galaska, "Electron Beam Curing of a Novel Liquid Crystal Thermoset Resin," *Thermochimica Acta*, 396 199-210, 2003.
9. M. Mascioni, J. Sands, G.R. Palmese, "Real Time In-situ Spectroscopic Characterizatoion of Radiation Induced Cationic Polymerization of Glycidyl Ethers," *Nuclear Instruments and Methods in Physics Research B*, 208,1-4, 353-357, 2003.

Proceedings and presentations:

1. J. Lee and G.R. Palmese, "Design and Umderstanding of EB Cured Epoxy Systems – Influence of Water on Cure Kinetics and Material Properties," *SAMPE 2006 Proceedings*, Long Beach, California, May, 2006.
2. M.E. Sullivan, D.A. Klosterman, and G.R. Palmese, " ," *SAMPE 2006 Proceedings*, Long Beach, California, May, 2006.
3. Klosterman, D., G. Karst, "A Study on the Reduction of Composite Warpage via E-beam Curing and a Subsequent Thermal Soak," *SAMPE 2006 Proceedings*, Long Beach, California, May, 2006.
4. J. Lee and G.R. Palmese, "Influence of Water on Cure Kinetics and Material Properties of DGEBA Epoxies Via UV and EB Irradiation," ACS Washington DC, PMSE, 2005
5. J. Lee and G.R. Palmese, "Design and Umderstanding of EB Cured Epoxy Systems – Influence of Water on Cure Kinetics and Material Properties," *Proceedings of the 50th International SAMPE Symposium*, Long Beach, May 1-5, 49, 2005.
6. J. Lee and G.R. Palmese, "Design of Improved Electron Beam Cured Epoxies," ASC/ASTM 19th Technical Conference Proceedings, Atlanta, GA, October 17-20, 2004.
7. X. Geng and G.R. Palmese, "Bismaleimide and Cyanate Ester Sequential IPN's for High Temperature Composite Liquid Molding Applications," ASC/ASTM 19th Technical Conference Proceedings, Atlanta, GA, October 17-20, 2004.
8. J.J. La Scala, J. Lee, C. Lee, J.M. Sands, G.R. Palmese, "The Use of E-Beam to Optimize the Properties of Fatty Acid-Based Polymers," *Proceedings of the 49th International SAMPE Symposium*, Long Beach, May 16-20, 49, 149-160, 2004.
9. Huh, W., J.Y. Kim, S. Lee, J-R Lee, D. Klosterman, "Synthesis of Epoxy Acrylate Pre-Polymers for Radiation Curing," *SAMPE 2004 Proceedings*, Long Beach, California, May, 2004.

10. J. Lee, A. Johnston, G.R. Palmese, "Dark and Light Reactions in EB Cationic Polymerization of Epoxies," *Proceedings of the 49th International SAMPE Symposium*, Long Beach, May 16-20, 49, 93-105, 2004.
11. L.G. Bykanova, C.A. Byrne, G.R. Palmese, "Electron Beam Cured Resins and Composites: Improved Two-Step Curing Materials for Cryogenic Applications," *Proceedings of the 49th International SAMPE Symposium*, Long Beach, May 16-20, 49, 161-171, 2004.
12. D.P. Anderson, D. Klosterman, G.R. Palmese, J. Lee, A. Johnston, A.J. Colleary, A. Desai, C.W. Lee, J.M. Brown, "Processing/Structure/Property Relationships of E-Beam Cured Cationic Epoxy," *Proceedings of the 49th International SAMPE Symposium*, Long Beach, May 16-20, 49, 119-132, 2004.
13. J. Lee and G.R. Palmese, "Dark and Light Reactions in EB Cationic Polymerization of Epoxies" *ACS Philadelphia, Polymer Preprints*, 45 (2), 10-11, 2004.
14. A. Johnston, K.C. Cole, L. Petrescue, G. Palmese, J. Lee, D. Klosterman, "Study of Reaction Kinetics of E-beam Cured Cationic Epoxy," *SAMPE 2004 Proceedings*, Long Beach, California, May, 2004.
15. D.A. Klosterman, A. Desai, "Development of a Model to Verify the Accuracy Of Thermocouples for Temperature Measurement During Electron Beam Curing of Polymers and Composites," *Proceedings of the 35th International SAMPE Technical Conference*, Dayton, Ohio, September 28-October 2, 2003.
16. E.J. Robinette, G.R. Palmese, "Radiation Grafting onto Electrospun Fibers," 226: 394-PMSE Part 2 SEP 2003.
17. X.Geng and G.R. Palmese, "Synthesis of Bismaleimide and Cyanate Ester Based Sequential IPN's Via EB Irradiation," *Proceedings of the 48th International SAMPE Symposium*, Long Beach, CA, May 11-15, 48, 1097-1108, 2003.
18. G.R. Palmese and G. Stein, "Influence of Water on UV and EB Induced Polymerization of Glycidyl Ethers," *Proceedings of the 48th International SAMPE Symposium*, Long Beach, CA May 11-15, 48, 2359-2369, 2003.
19. Klosterman, D.A. "Characteristics of an Electron Beam Used For Basic Research Studies on Composite Curing", *Proceedings of the 48th International SAMPE Symposium & Exhibition*, Long Beach, CA, May 11-15, 2003.

Thesis and Dissertation:

1. J. Lee, "Design of Improved EB-Cured Epoxy Systems," PhD, anticipated completion: September 2006
2. X. Geng, "Design of EB-Cured Cyanate Ester-Bismaleimide Sequential Interpenetrating Polymer Networks (IPNs) for High Temperature Applications," Ph.D. Dissertation, Drexel University, Awarded PhD June 2005.
3. A. Desai, "Development of A Simple Calorimeter for Measuring Polymer Cure Rate and Radiation Dose During E-beam Irradiation," MS Thesis, University of Dayton, December 2004.

7.0 Interactions/Transitions

a. participation in meetings, conferences, seminars (*in addition to those related to the proceedings outlined above*)

Talks:

- G.R. Palmese, "Radiation Grafting for Surface Modification of Nanofibers," SPE-ANTEC Conference, New Technology Forum – Radiation Processing of Polymers, May 17 2004, Chicago IL - invited
- G.R. Palmese, X.Geng, J. Lee, "Real-Time In-situ Characterization of EB Cured Polymers for High Temperature Applications," High Temple, Sacramento CA February 2-5, 2004 – invited
- E.J. Robinette, G.R. Palmese, "Radiation Grafting onto Electrospun Fibers," AIChE Annual Meeting, San Francisco, CA, November 16-21, 2003.
- Klosterman, D.A., "Thermal Analysis of Thermoset Resins Cured in the Solid State by Electron Beam Irradiation," presented at the 31st North American Thermal Analysis Society Conference," Albuquerque, New Mexico, September 22-24, 2003
- Klosterman, D.A., "Thermal Analysis of Thermoset Resins Cured in the Solid State by Electron Beam Irradiation," invited presentation, Ohio Valley Thermal Analysis Society Meeting, October 16, 2003, Cincinnati, Ohio.
- G.R. Palmese, "Characterization of Radiation-Induced Thermoset Cure, NaTex, Challenges in Materials Characterization," Second Annual Symposium, Houston, Texas April 25-26, (2003) – invited
- G.R. Palmese, "Radiation Grafting – A Unique Method of Modifying Surface and Bulk Polymer Properties, Radiation Processing for Polymers of the 21st Century, IBA Conference," Philadelphia PA, April 8-9 (2003) - invited.
- M. Mascioni, J.M. Sands and G.R. Palmese, "Spectroscopic Characterization of UV and EB Induced Epoxy Polymerization" IRAP, Montreal Canada September 22-25, 2002

Conference Sessions Chaired:

- G.R. Palmese, Session Chairman, Electron Beam Processing II, SAMPE 2004 Annual Meeting.
- G.R. Palmese, Session Vice-Chair, Electron Beam Processing I, SAMPE 2004 Annual Meeting.

b. Interactions with AFRL, NRC, Texas A&M and Soongsil University

A Table of important collaborative interactions involving the EB facility and other associated listed events are given below and include the following collaborators:

AFRL – Janis Brown
NRC – Andrew Johnston, Laura Petrescue
McGill University - Dr. Przemyslaw Pazdzior, Professor Pascal Hubert
Soongsil University - Professor Wansoo Huh
Cornerstone Research Group - Dr. Pat Hood, Dr. Tat Tong
Boeing, Seattle - Dr. Mark Welinski
Boeing, Philadelphia – Mr. Karl Bernetich
Texas A&M – Roger Morgan

Summary of Interactions / Collaborations

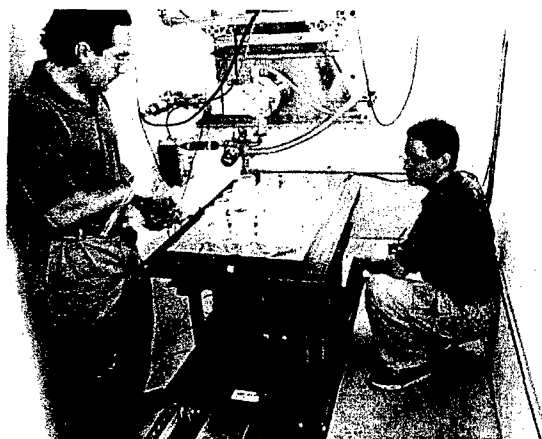
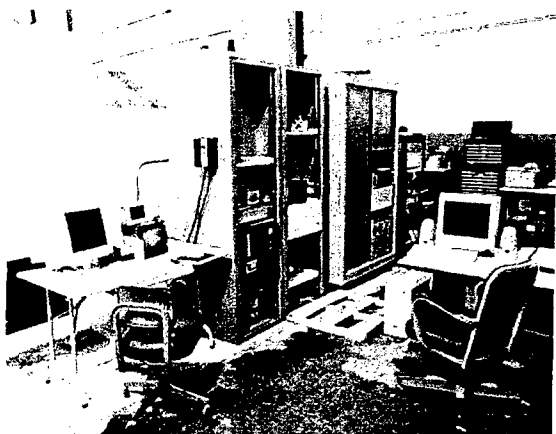
- Dr. Janis Brown, AFRL/MLBC, structure-processing-property relationships of e-beam cured epoxy resins.
- Mr. Kirk Ziegler, Rice University, “use of e-beam radiation for scission of single wall nanotubes (SWNT)”. The goal is to create seed tubes for controlled nanotube nucleation. Results demonstrated improved ability to obtain more highly uniform tube size for seed growth.
- Professor Wansoo Huh, Soongsil University, Korea, “e-beam curing of thermoset resins for composite applications”. On-going collaboration involves use of e-beam calorimeter to study kinetics of vinyl ester resins, unsaturated polyester resins, and hyperbranched polymer modified resins. Highlights include 2-week visit by Korean Ph.D. student during August 2004. Joint publications will be forthcoming.
- Dr. Andrew Johnston, National Research Council of Canada (NRC), “use of e-beam calorimetry to elucidate epoxy cure kinetics”. Collaboration involved use of NRC’s foam-insulated calorimeter to study epoxy resin cure under e-beam irradiation. Highlights include the first comparisons of calorimeter kinetic data to independent spectroscopic kinetic data for epoxy resin cure. (joint publications – see SAMPE 2004 proceedings, joint journal publication forthcoming)
- Dr. Przemyslaw Pazdzior, Professor Pascal Hubert, McGill University, Canada, “in-situ monitoring of residual stress development during e-beam cure of epoxy resin”. Collaboration involved use of a novel fixture to study levels of residual stress in epoxy resins in real time during e-beam cure. Highlights include landmark study quantifying low residual stress and warpage as an inherent benefit of e-beam curing. Continued study and publication expected.
- Professor C. William Lee, University of Dayton, “development of a calorimeter for real-time monitoring of polymer cure kinetics during e-beam irradiation”. Highlights include developing novel concept to refine NRC’s foam calorimeter for improved accuracy, ease of set-up, and analytical computation.
- Dr. Pat Hood, Dr. Tat Tong, Greg Karst, Cornerstone Research Group,
 - “e-beam cured materials for composite mirrors” Phase I STTR program. Highlights include implementing techniques to further quantify reduced residual stress and warpage in e-beam cured resins.
 - Shape memory alloys

- Interaction with Boeing Seattle with Dr. Marl Welinki to design improved free radically cured resin system. Resin was prepregged and tested by Boeing and performed well.
- Helped Karl Bernetich (Boeing Philadelphia) understand the cure behavior and properties of cationically EB cured DGEBA based epoxies.

Activity ^{1,2}	Topic Studied	Collaborators	Dates
Planning meeting	Program	AFRL, UDRI	11/2002
E-beam marathon	Spectroscopy	UDRI, Drexel, AFRL/MLBC	3/25-3/28/2003
E-beam exposure service and study	Calorimeter implementation	NRC, AFRL, UDRI	3/26, 6/12, 6/26, 7/3/2003
E-beam marathon	Calorimeter & residual stress	Drexel, AFRL, Texas A&M, Army Research Lab, NRC, Soongsil Univ.	7/9-7/11/2003
E-beam exposure service and study	Cationic epoxy curing	AFRL/MLBC	7/24/2003
E-beam marathon	Spectroscopy	Drexel, AFRL/MLBC	8/25-8/27/2003
E-beam marathon	Residual stress, calorimetry of cationic epoxy	Drexel, AFRL/MLBC, AFOSR, Boeing, NRC, McGill, Soongsil	October 2004
SWNT irradiation	Nanotube modification	Rice University	Dec. 2003, March 2004, Sept. 2004
NIR spectroscopy of cationic epoxy	Influence of water	Drexel University	Jan. 2004
Cure studies	Cationic epoxy curing	AFRL/MLBC	Oct. 2004-Jan. 2004
Free radical cured systems	Vinyl ester and polyester resin calorimetry and resin curing	Soongsil	August 2004 (2 weeks)
Various resin cure trials	Warpage and shape memory	Cornerstone Research Group	Sept. 2004

¹ "E-beam marathon" indicates when visitors outside of UDRI and AFRL/MLBC were present for focused day(s) of collaborative hands-on research and discussion at the UDRI facility² "E-beam exposure service and study" are days when UDRI and AFRL/MLBC researchers worked together in the UDRI facility to cure materials and gather real-time sensor data. On these days, calorimeter data was sent to NRC via email for review.

Illustrations



UDRI e-beam facility

“E-beam Marathon”, October 2003





Collaborators from Drexel, UDRI, Texas A&M, AFRL, NRC and ARL during July 2003
"E-beam Marathon" week.

8.0 New Discoveries

Preparation in progress of patent Disclosure, G.R. Palmese and J. Lee, "Novel THF terminated Monomers for Toughening Radiation Cured Glycidyl Epoxy Systems, "

9.0 Honors and Awards

None